

(12) **UK Patent Application** (19) **GB** (11) **2 321 470** (13) **A**

(43) Date of A Publication **29.07.1998**

(21) Application No **9725909.7**

(22) Date of Filing **09.12.1997**

(30) Priority Data

(31) **9700909** (32) **17.01.1997** (33) **GB**  
(31) **9707665** (32) **16.04.1997**

(71) Applicant(s)

**T & N Technology Limited**  
(Incorporated in the United Kingdom)  
**Cawston House, Cawston Lane, RUGBY,**  
**Warwickshire, CV22 7SA, United Kingdom**

(72) Inventor(s)

**Alan William Atkinson**  
**Stephen Peter Bond**  
**Darryl Alfred Turland**  
**Paul Reuben Percival**

(74) Agent and/or Address for Service

**P L Drury et al**  
**T & N Plc, Group Patent Department, Bowdon House,**  
**Ashburton Road West, Trafford Park, MANCHESTER,**  
**M17 1RA, United Kingdom**

(51) INT CL<sup>6</sup>

**C09K 3/10, F16J 15/10**

(52) UK CL (Edition P)

**D1R RDC R162 R303 R602 R612**  
**C3V VDS VEK**  
**C3W W327**  
**U1S S1782 S1990**

(56) Documents Cited

**US 5232973 A**  
**WPI Abstract Accession No. 90-234427/31 & JP**  
**020160891A WPI Abstract Accession No.**  
**88-129625/19 & JP 630072780A**

(58) Field of Search

**UK CL (Edition P) C3K KMA, C3V VBX VDS VDT**  
**VEK, D1R RBX RDC RDP RFA**  
**INT CL<sup>6</sup> C09K 3/10 3/12, F16J 9/26 15/10 15/20, F16K**  
**41/04**  
**Online: WPI**

(54) Abstract Title

**Sealing material**

(57) Sealing material comprises from 45-90% by weight exfoliated graphite, from 5 to 20% by weight thermosetting resin, and from 5 to 50% by weight fibrous filler which is heat resistant at 250°C. The fibrous filler has fibres at least 90% of which have a fibre length of less than 200µm, and an aspect ratio of less than 10:1. The fibrous filler may be wollastonite and the resin may be phenolic.

**GB 2 321 470 A**

### SEALING MATERIAL

The invention relates to a sealing material comprising exfoliated graphite, thermosetting resin, and a fibrous filler.

Sealing materials comprising exfoliated graphite have been used as cylinder head gaskets and other types of seals in internal combustion engines, such as automobile engines for some time, since they have good heat resistance and stress relaxation properties. Graphite sheets have been found to have poor resistance to oil, and this has restricted their use. Means have been sought to improve the oil resistance of graphite sheets. Japanese patent application number 63-72780 relates to a graphite sheet which has expanded graphite particles, heat-resistant fibres, and an organic high-polymer binder as principal components. The graphite sheets produced are said to have improved oil resistance and antifreeze resistance. Heat-resistant inorganic fibres such as rockwool, ceramic fibres, silicate fibres and surface-treated silicate fibres or heat-resistant organic fibres such as aromatic polyamide fibres and phenolic resin fibres can be used as the heat-resistant fibres. The length of the heat-resistant fibres is said to be about 1-50mm, and the thickness from 10-300 $\mu$ m.

In use, when a sealing material comprising exfoliated graphite is under pressure, extrusion of the material may occur jeopardizing the seal. This occurs considerably more easily when the graphite is oil-soaked than in an oil-free environment. Since such extrusion is an undesirable characteristic, it is desirable that extrusion of sealing

material is avoided at pressures ordinarily experienced by them in oily environments. The pressure at which extrusion occurs (the extrusion collapse point) should be above such pressures.

According to the present invention, there is provided sealing material comprising from 45-90% by weight exfoliated graphite, from 5 to 20% by weight thermosetting resin, and from 5 to 50% by weight fibrous filler which is heat resistant at 250°C, the fibrous filler having fibres at least 90% of which have a fibre length of less than 200µm, and an aspect ratio of less than 10:1.

It has surprisingly been found that, sealing materials comprising fibrous fillers with the short fibre lengths and aspect ratios of the present invention, have considerably higher extrusion collapse points, than sealing elements of graphite foil comprising exfoliated graphite alone, than graphite foil with phenolic resin, or than graphite foil comprising phenolic resin and fibrous fillers having fibre lengths of similar size to those described in JP 63 72780. In some embodiments, the sealing material is in the form of a sheet or layer, for example, of a planar gasket such as an automotive head gasket.

In other embodiments the sealing material is in the form of a moulded shape, such as a shaft sealing ring.

A sealing material according to the invention may comprise from 5 to 20% by weight of the thermosetting resin, and from 5 to 30% by weight of the fibrous filler.

Conveniently, the thermosetting resin is a phenolic resin.

When a filler is used in which at least 90% of the fibres of the fibrous filler have a fibre length of less

than  $20\mu\text{m}$ , a further increase in the extrusion collapse point is found, and so it is preferred to use fibres of this length. Use of a fibrous filler at least 90% of the fibres of which have a fibre length of less than  $10\mu\text{m}$  is more preferable.

Advantageously, the aspect ratio of the fibrous filler is less than 6:1.

The exfoliated graphite is mixed with the fibrous filler (and, optionally, the powdered thermosetting resin) in the dry state, eg by gentle tumbling or in the airborne state. A layer of the mixture is then compacted, usually by passage between rollers, to form a coherent foil or sheet. Alternatively, the mixture may be compacted to other shapes eg sealing rings. Such other shapes may also be made by re-moulding foil.

When the resin is added as a free-flowing powder, it may subsequently be made to flow, prior to cross-linking, by heating the consolidated foil (optionally under pressure). Further heating, normally to a higher temperature, then cross-linking the resin.

Alternatively, the powdered resin can be made to distribute itself more effectively through the foil by soaking in solvent and then drying.

A preferred method of introducing resin is to initially compress the exfoliated graphite to a relatively low density (eg  $0.5\text{kg m}^{-3}$ ) so that some porosity is maintained. Liquid resin (solution or suspension in water, etc) is then allowed to soak in. After drying, the low density foil is compressed further to achieve the required final density.

The graphite sheet preferably has a final density of from 0.7 to 1.5 kg m<sup>3</sup>. Final densities of less than 0.7 are too weak and compressible. Densities of over 1.5 tend to be too hard and incompressible, giving a poor seal.

A particularly preferred fibrous filler is wollastonite the fibre length of which falls within the ranges of the present invention.

In addition to increasing the stress at which extrusion begins, shorter fibres and lower aspect ratios make it easier to mix the fibrous filler with the exfoliated graphite. This gives a more homogeneous product, which may contribute to improved performance.

A particular application of the sealing element of the present invention is used in a multi-layer steel gasket in the form of a thin coating on the gasket to fill fissures. Typically, such a sealing element will be in the range from 50 to 100µm thick, preferably approximately 75µm thick.

In another application of the sealing element, a graphite layer or sheet from 0.5 to 2mm thick may be provided which acts to provide resilience in a gasket.

#### Comparative Example 1

Graphite foil having a thickness of approximately 200µm was formed by conventional means from expanded graphite. The graphite foil was consolidated by passing through calenders to achieve a foil thickness of 75µm and a final density of 1.4 kg m<sup>3</sup>.

#### Comparative Example 2

Graphite foil having a final thickness of approximately 200µm as formed in the first stage of comparative example 1 but with an intermediate density of 0.5 kg m<sup>3</sup> was impregnated with approximately 10% phenolic

resin by first passing the foil through a bath containing a resole phenolic resin, Borden<sup>(R.T.M.)</sup> SC1008 resin in methyl isobutylketone solvent, and then by drying in an oven. The resin-impregnated graphite foil was then further consolidated as in comparative example 1.

### Comparative Example 3

Graphite foil comprising approximately 10% by weight of mica was formed as in comparative examples 1 and 2 except that 10% of mica was added to the graphite prior to the expansion stage in the furnace. The foil was then impregnated and consolidated as in comparative example 2.

### Comparative Examples 4 and 5

Comparative example 3 was repeated except that the graphite foil comprised (in Comparative Example 4) 10% of Nygloss wollastonite having a median fibre length of 0.25mm or (in Comparative Example 5) Franklin Fibre (calcium sulphate ex Franklin Institute with a length of about 1mm) instead of Mica. When it was attempted to make a graphite foil of 75 $\mu$ m thickness, the fibres coagulated and a foil was unable to be formed. The product was weak and inhomogeneous and would not form a satisfactory seal.

There now follow examples 1 to 6 which are illustrative of the present invention.

### Example 1

Comparative example 3 was repeated except that the graphite foil comprised 10% of wollastonite instead of mica.

(R.T.M.)

The wollastonite incorporated was Wollastocoat<sub>10</sub> (from Nyco minerals), having an aspect ratio of 3:1, a median fibre length of 3 $\mu$ m, 96% of the fibres having a length below 10 $\mu$ m.

#### Example 2

Example 1 was repeated except that the wollastonite was Nyad<sup>(R+M)</sup> 400 (from Nyco minerals) having an aspect ratio of 5:1 and a median fibre length of approximately 25 $\mu$ m.

#### Example 3

Example 1 was repeated except that the wollastonite was Vansil EW10 (from Vanderbilt, UK distributor, Microfine Minerals), having an aspect ratio of between 5:1 and 10:1, a median fibre length of approximately 32 $\mu$ m, 97% of the fibres having a length below 63 $\mu$ m, and 40% below 20 $\mu$ m.

#### Example 4

Example 1 was repeated except that the woolastonite fibres formed 22% by weight and the final density was 1.1.

#### Example 5

Example 1 was repeated except that the woolastonite fibres formed 24% by weight and the phenolic resin formed 18% by weight. The final density was 1.4.

#### Example 6

Example 1 was repeated except that the woolastonite fibres formed 24% by weight and the phenolic resin formed 9% by weight. The final density was 1.4.

Tests were carried out on the products of the foils produced in the examples and the comparative examples as follows.

Each foil sample was soaked in a standard oil (ASTM oil 3) at 150°C for 5 hours. The foils were then subjected to pressure, to find their extrusion collapse points, that is the pressure at which extrusion occurs after the foils have been soaked in oil.

The results were as follows:

Extrusion collapse point (MPa)	
Comparative Example 1	85
Comparative Example 2	87
Comparative Example 3	87
Comparative Examples 4 and 5	could not be determined
Example 1	122
Example 2	99
Example 3	98
Example 4	164
Example 5	186
Example 6	155

This shows that the inclusion of the wollastonite of short fibre length as in examples 1 to 6 significantly raises the extrusion collapse point in this test.



## CLAIMS

- 1     Sealing material comprising from 45-90% by weight exfoliated graphite, from 5 to 20% by weight thermosetting resin, and from 5 to 50% by weight fibrous filler which is heat resistant at 250°C, the fibrous filler having fibres at least 90% of which have a fibre length of less than 200 $\mu$ m, and an aspect ratio of less than 10:1.
- 2     Sealing material according to claim 1, wherein the material comprises from 5 to 20% by weight of the thermosetting resin, and from 5 to 30% by weight of the fibrous filler.
- 3     A sealing material as claimed in either one of claims 1 and 2, wherein the thermosetting resin is a phenolic resin.
- 4     A sealing material as claimed in any one of claims 1 to 3, wherein at least 90% of the fibres of the fibrous filler have a fibre length of less than 20 $\mu$ m.
- 5     A sealing material as claimed in claim 4, wherein at least 90% of the fibres of the fibrous filler have a fibre length of less than 10 $\mu$ m.
- 6     A sealing material as claimed in any one of the preceding claims, wherein the aspect ratio of the fibres of the fibrous filler is less than 6:1.
- 7     A sealing material as claimed in any one of the preceding claims, wherein the fibrous filler is wollastonite.

- 8 A sealing material as claimed in any one of the preceding claims, wherein the sealing material is in the form of a sheet or layer.
- 9 A sealing material as claimed in any one of the preceding claims, wherein the sheet or layer has a thickness of from  $50\mu\text{m}$  to  $100\mu\text{m}$ .
- 10 A sealing material as claimed in any one of claims 1 to 7, wherein the sealing material is in the form of a moulded shape.
- 11 A sealing material as claimed in any one of the preceding claims, wherein the sealing material has a density of from  $0.7$  to  $1.5\text{kgm}^{-3}$ .
- 12 A sealing material substantially as hereinbefore described, with reference to example 1, 2, 3, 4, 5 or 6.



Application No: GB 9725909.7  
Claims searched: 1-12

Examiner: Alex Littlejohn  
Date of search: 2 March 1998

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK Cl (Ed.P): C3V (VBX, VDS, VDT, VEK); C3K (KMA); D1R (RBX, RDC, RDP, RFA)  
Int Cl (Ed.6): C09K 3/10, 3/12; F16J 9/26, 15/10, 15/20; F16K 41/04  
Other: Online: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
A	US5232973 (Toyota) see e.g. claim 1	-
A	WPI Abstract Accession No. 90-234427/31 & JP 020160891A (Nippon Gasket) 20.06.90 see abstract	-
A	WPI Abstract Accession No. 88-129625/19 & JP 630072780A (Nippon Reinz) 02.04.88 see abstract	-

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

